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(54) 【発明の名称】 弗素高含有ガラスの製造方法

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【特許請求の範囲】

【請求項 1】 弗素高含有ガラスを製造するに当たり、バッチ原料熔融後生成されたガラス体の存在下において、アニオンック % で 0.0001 ~ 0.1 % 未満の塩素、沃素および臭素の 1 種以上の成分を添加した後、脱泡均質化することを特徴とする弗素高含有ガラスの製造方法。

【発明の詳細な説明】

【産業上の技術分野】

本発明は、白金等の貴金属製のガラス熔融容器の劣化損傷を防止しつつ、実質的に泡や容器溶出物のない高品質の弗燐酸塩ガラスや弗化物ガラス等の弗素高含有ガラスを製造する方法に関する。

【従来の技術】

従来、上記の弗素高含有ガラスの用途として、光学用ガラス、フィルターガラスおよびレーザー用ガラス等が

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知られている。しかし、これらのガラスは、熔融中に微小泡が多数発生し、これが消失し難いため、製品中に残留して品質を著しく低下させる欠点がある。

一般に、ガラスの脱泡方法としては、As₂O₃ や Sb₂O₃ 等の清澄剤を添加した粉末バッチ原料を熔融する方法が知られているが、弗素高含有ガラスの場合は、熔融温度が低い場合、この方法を用いても殆ど効果がない。上記問題の解決を試みたガラスとして、たとえば特開昭 55 - 109242 号公報には、沃素および / または臭素を 0.1 アニオンック % 以上添加してなる弗燐酸塩ガラスが開示されている。この公報には、上記成分の具体的添加方法について、何ら開示されていないが、添加量が多いため、ガラス熔融の際、これらの成分が白金等の容器を侵して次第に脆化させ、また容器にクラック等の損傷を招きやすい欠点がある。また、上記容器の脆化損傷は、ガラスの汚

染原因となり、その品質を劣化させやすい。

〔発明が解決しようとする問題点〕

本発明は、上記の状況にかんがみてなされたもので、その目的とするところは、熔融容器の脆化損傷を防止しつつ、脱泡均質化を行い、実質的に微小泡や容器からの溶出物のない高品質の弗素高含有ガラスを製造する新規な方法を提供することにある。

〔問題点を解決するための手段〕

本発明者は、上記目的を達成するため鋭意試験研究を重ねた結果、弗素高含有ガラスの製造に当たり、清澄剤の添加を通常行なわれる多成分調合粉末原料（バッチ原料）中に添加するのではなく、バッチ原料熔融後生成するガラス体の存在下において塩素および／または沃素および／または臭素を添加する場合は、意外にも、これらの成分の添加量は、極めて少量で所期の効果が得られることをみだし、本発明をなすに至った。

本発明にかかる弗素高含有ガラスの製造方法は、特許請求の範囲に記載のとおり、弗素高含有ガラスを製造するに当り、バッチ原料熔融後生成されたガラス体の存在下において、アニオニック%で0.0001～0.1%未満の塩素、沃素および臭素の1種以上の成分を添加した後、脱泡均質化することを特徴とする。

上記添加剤のガラス中の含有量の総量は、上記熔融容器の浸食脆化を防止し、かつ、所望の清澄均質化効果を得るため、アニオニック%で、0.0001～0.1%未満、好ましくは0.001～0.1%未満であることが必要である。なお、本発明の方法において、ガラスの熔融雰囲気は、必要に応じ、中性または酸化性等の雰囲気を適宜選び得

表

る。また、上記添加剤は、固状ないし液状の状態下にある上記ガラス体に適宜添加し得る。

〔実施例〕

つぎに、本発明の方法を実施例にもとづき説明する。

本発明の方法の実施に当っては、実質的に、カチオニック%で、 $1/2P_2O_5$ 0～60%、 PF_5 0～20%、 $R^I F$ ($LiF + NaF + KF$ 等) 0～40%、 $R^{II} F$ ($MgF_2 + CaF_2 + SrF_2 + BaF_2 + ZrF_4 + PbF_2$ 等) 10～70%、 $R^{III} F$ ($AlF_3 + YF_3 + LaF_3$ 等) 5～45%、 $R^{IV} F$ ($ZrF_4 + HfF_4$ 等) 0～30%、 $1/2B_2O_3$ 0～30%、 $1/2Nd_2O_3$ 0～5%の組成を有する弗素高含有ガラスを基礎として使用することが好ましい。表-1は、その好適な基礎ガラス組成（比較例）と本発明の方法により、この基礎ガラスに塩素（Cl）、沃素（I）および臭素（Br）を外割添加して得られるガラス組成例とについて、脱泡状況比較試験結果とともに示したものである。

表記のガラスが得られるように調合したバッチ原料を炉内白金るつぼ中に投入し、組成による熔融の難易度に応じて900～1150℃でバッチがかなり残存するもガラス化してガラス体が存在する状態に粗熔融した後、炉温を約550～700℃に低下し、熔融ガラス中にCl、IおよびBrを表記のアニオニック%量で外割添加して攪拌混合する。ついで、再度炉温を900～1150℃に上げ脱泡均質化処理を行なった後、再び炉温を500～700℃に下げガラスを鋳型に鋳込みブロックを得る。

これらの実施例および比較例により得られたブロックを研磨し、ガラス100ml中の泡の断面積を測定し、その総和A (mm²)を求めたところ、表記の結果を得た。

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(cat.%)

	I	1	2	II	3	4	III	5	6	IV	7	8	V	9	10
$1/2P_2O_5$	34.3			27.3			18.0			14.0					
AlF_3	20.6			23.1			30.0			30.7			34.6		
MgF_2	1.7						6.0			6.0			6.4		
CaF_2	22.0			20.5			18.0			24.5			20.5		
SrF_2	13.9			20.6			8.0			16.8			9.5		
BaF_2	7.5			8.3			8.0			6.9			6.4		
その他				PbO			0.2			NaF			10.0		
							M_2O_3			YF_3			0.9		
							$1/2Nd_2O_3$			KF			0.2		
										PF_5			2.3		
										SiF_4			6.5		
										YF_3			5.5		
										LaF_3			4.1		
										NaF			2.4		
										KF			1.8		
添加剤	Cl	0	0.05	0	0	0	0	0	0.01	0	0	0	0	0	0
	I	0	0	0.01	0	0.001	0	0	0	0	0	0.08	0.01	0	0
	Br	0	0	0	0	0	0.03	0	0	0.01	0	0	0.01	0	0.02

	I	1	2	II	3	4	III	5	6	IV	7	8	V	9	10
A($\text{mm}^2/100\text{ml}$)	1.5	0.05	0	1.3	0.08	0.05	2.5	0.1	0.05	3.2	0	0.05	5.5	0	0.05

表にみられるとおり、本発明の方法により得られるガラスのA値は、0.08以下であるのに対し、比較例の各ガラスのA値は、いずれも1.3以上であり、両各例の差は顕著であると認められる。

以上、本発明の実施例につき説明したが、本発明は、上記実施例の方法に限定されるものではなく、たとえば、添加剤の添加に際しては、バッチ原料を完全にガラス化させた後の熔融ガラス体に添加してもよく、あるいは、ガラスカレットを必要に応じバッチ原料とともに再生利用する過程で添加してもよく、本発明の技術思想を逸脱しない範囲で適宜改変しうる。

なお、本発明の方法により得られる弗素高含有ガラス

中に含まれる上記添加剤の量は、比較的微量であるが、高精度で検出測定可能であるので、最適添加含有量を工程管理することが可能である。

〔発明の効果〕

上述のとおり、本発明にかかる弗素高含有ガラスの製造方法は、ガラス化状態のガラス体の存在化において、アニオニック%で0.0001~0.1%未満の微量の塩素、沃素および臭素の1種以上の成分を添加した後、脱泡均質化する構成であるから、泡と貴金属溶出粒子が実質的にない光学用、フィルター用およびレーザー用等の弗燐酸塩ガラスや弗化物ガラスを安定して取得し得る。

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(col. 3, line 22 ~ col. 4, line 1)

The total amount of the above additives (chloride, isodide and bromide) in the glass is not less than 0.0001% and less than 0.1%, expressed in terms of anionic %, preferably not less than 0.001% and less than 0.1% in order to prevent the above melting vessel from corroding and embrittling, and obtain the desired refining and homogenizing effect. In the present invention, the glass melting atmosphere is suitably selected among neutral atmosphere and oxidizing atmosphere, etc.

(col. 6, lines 9-15)

As stated above, according to the present invention of the method for producing glass with a high fluorine content, since one or more components of chlorine, iodine and bromine in an amount of 0.0001 to 0.1% expressed in terms of anionic % are added to the molten glass in the glassified state, and then defoaming and homogenization treatment is carried out, it is possible to produce fluorophosphate glass and fluoride glass which is substantially free from bubbles and eluted precious metal particles. These glasses are used as optical glass, optical filter glass and laser glass.

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CLAIMS

[Claim(s)]

[Claim 1] the bottom of existence of the vitreous humour generated after batch raw material melting in manufacturing fluorine quantity content glass -- setting -- Anio -- the manufacture method of the fluorine quantity content glass characterized by carrying out degassing homogenization after adding one or more sorts of components of less than 0.0001 - 0.1% of chlorine, an iodine, and a bromine by nick %

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Industrial Application]

this invention relates to the method of manufacturing the fluorine quantity content glass which has neither a bubble nor a container effluent substantially, such as quality ***** and a fluoride glass, preventing the degradation damage on the glass melting container made from noble metals, such as platinum.

[Description of the Prior Art]

Conventionally, the glass for optics, a filter lens, the glass for laser, etc. are known as a use of the above-mentioned fluorine quantity content glass. However, since many minute bubbles are generated during melting and this cannot disappear easily, these glass has the fault in which it remains in a product and quality is reduced remarkably.

Although the method of generally fusing the powder batch raw material which added the clarifier of As₂O₃ or Sb₂O₃ grade as the degassing method of glass is learned, since melting temperature is low, even if it uses this method, in the case of fluorine quantity content glass, it is almost ineffective. As glass which tried solution of the above-mentioned problem, ***** which comes to add an iodine and/or a bromine more than nick % 0.1 Anio is indicated by JP,55-109242,A. Although not indicated at all about the concrete addition method of the above-mentioned component by this official report, since there are many additions, in case it is glass melting, it has the fault which these components invade containers, such as platinum, and is made to carry out an embrittlement gradually, and is easy to invite the damage on a crack etc. to a container. Moreover, the embrittlement damage on the above-mentioned container causes [of glass] pollution, and is easy to degrade the quality.

[Problem(s) to be Solved by the Invention]

Preventing the embrittlement damage on a melting container, the place which this invention was made in view of the above-mentioned situation, and is made into the purpose performs degassing homogenization, and is to offer the new method of manufacturing the quality fluorine quantity content glass which does not have an effluent from a minute bubble or a container substantially.

[Means for Solving the Problem]

In order that this invention person may attain the above-mentioned purpose, as a result of repeating test research wholeheartedly, it does not add in manufacture of fluorine quantity content glass in the multicomponent preparation powder raw material (batch raw material) which has a clarifier usually added. when adding chlorine, an iodine, and/or a bromine under existence of the vitreous humour generated after batch raw material melting, the expected effect that the addition of these components is very little also unexpectedly is acquired -- **** -- it takes out and came to make this invention the bottom of existence of the vitreous humour generated after batch raw material melting in case the manufacture method of the fluorine quantity content glass concerning this invention manufactured fluorine quantity content glass as given in a claim -- setting -- Anio -- after adding one or more sorts of components of less than 0.0001 - 0.1% of chlorine, an iodine, and a bromine by nick %, it is characterized

by carrying out degassing homogenization

in order for the total amount of the content in the glass of the above-mentioned additive to prevent the corrosion embrittlement of the above-mentioned melting container and to acquire the desired clear homogenization effect -- Anio -- it nick % comes out and it is required to be less than 0.001 - 0.1% preferably less than 0.0001 to 0.1% In addition, in the method of this invention, the melting atmosphere of glass can choose atmosphere, such as neutrality or an oxidizing quality, suitably if needed. Moreover, the above-mentioned additive can be suitably added to the above-mentioned vitreous humour under a solid state or a liquefied state.

[Example]

Below, the method of this invention is explained based on an example.

In operation of the method of this invention, it is cationic % substantially. $1/2P_2O_5$ 50-60%, 50 - 20% of PFs, 0 - 40% (LiF+NaF+KF etc.) of RIF, 10 - 70% ($MgF_2+CaF_2+SrF_2+BaF_2+ZnF_2+PbF_2$ grade) of RIIF(s), Be based on 5 - 45% ($AlF_3+YF_3+LaF_3$ grade) of RIIF(s), 0 - 30% (ZrF_4+HfF_4 grade) of RIVF(s), $2O_3O$ - 30% of $1/2Bs$, and the fluorine quantity content glass that has composition of $2O_3O$ - 5% of $1/2Nd(s)$. It is desirable to use it. Table -1 is shown with a degassing situation comparison test result about the example of glass composition acquired by this base glass by carrying out outside rate addition of chlorine (Cl), an iodine (I), and the bromine (Br) by the method of of the suitable base-glass composition (example of comparison) and suitable this invention.

the coke oven temperature after rough-fusing in the state in which throws in the batch raw material prepared so that declared glass might be obtained in the platinum crucible in a furnace, and a batch carries out remarkable survival at 900-1150 degrees C according to the difficulty of melting by composition where of carry out ** vitrification and a vitreous humour exists -- about 550-700 degrees C -- falling -- Anio of notation of Cl, I, and Br in melting glass -- outside rate addition carries out and churning mixture carries out in the amount of nick %s Subsequently, after raising a coke oven temperature to 900-1150 degrees C again and performing degassing homogenization, a coke oven temperature is again lowered to 500-700 degrees C, glass is cast to mold, and a block is acquired.

the block acquired by these examples and the example of comparison -- grinding -- glass 100ml -- the result of the notation was obtained, when the cross section of an inner bubble was measured and having been asked for the total A (mm²)

表

1

(cat.%)

	I	1	2	II	3	4	III	5	6	IV	7	8	V	9	10
$1/2P_2O_5$	34.3			27.3			18.0			14.0					
AlF_3	20.6			23.1			30.0			30.7			34.6		
MgF_2	1.7						6.0			6.0			6.4		
CaF_2	22.0			20.5			18.0			24.5			20.5		
SrF_2	13.9			20.6			8.0			16.8			9.5		
BaF_2	7.5			8.3			8.0			6.9			6.4		
その他				PbO 0.2			NaF 10.0 MnO_3 2.0 $1/2Nd_2O_3$ 2.0			YF ₃ 0.9 KF 0.2			PF ₅ 2.3 SiF ₄ 6.5 YF ₃ 5.5 LaF ₃ 4.1 NaF 2.4 KF 1.8		
添加剤	Cl	0	0.05	0	0	0	0	0.01	0	0	0	0	0	0	0
	I	0	0	0.01	0	0.001	0	0	0	0	0	0.08	0.01	0	0.01
	Br	0	0	0	0	0	0.03	0	0	0.01	0	0	0.01	0	0.02

	I	1	2	II	3	4	III	5	6	IV	7	8	V	9	10
$A(mm^2/100ml)$	1.5	0.05	0	1.3	0.08	0.05	2.5	0.1	0.05	3.2	0	0.05	5.5	0	0.05

To A value of the glass obtained by the method of this invention being 0.08 or less as it sees in a table, each A value of each glass of the example of comparison is 1.3 or more, and it is admitted that the difference of the example of both ** is remarkable.

As mentioned above, although explained per example of this invention, you may add in the process which is not limited to the method of the above-mentioned example, and may add to the melting vitreous humour after making [for example,] a batch raw material vitrify completely on the occasion of addition of an additive, or carries out the reuse of the glass caret with a batch raw material if needed, and this invention can be suitably changed in the range which does not deviate from the technical thought of this invention.

in addition -- although the amount of the above-mentioned additive contained in the fluorine quantity content glass obtained by the method of this invention is a minute amount comparatively -- highly precise -- detection -- since it is measurable, it is possible to control a process in the optimal addition content [Effect of the Invention]

The manufacture method of the fluorine quantity content glass applied to this invention as above-mentioned, existence[the vitreous humour of a vitrification state]-izing -- setting -- Anio -- since it is the composition which carries out degassing homogenization after adding one or more sorts of components of the chlorine of less than 0.0001 - 0.1% of minute amount, an iodine, and a bromine by nick %, it is stabilized and ***** and the fluoride glasses the object for optics which does not have a bubble and a noble-metals elution particle substantially, the object for filters, for laser, etc. can be acquired